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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Monoethanolamine Impregnated Activated Carbon and uses thereof

- We, PITTSBURGH ACTIVATED CARBON COMPANY, a Corporation of the State of Pennsylvania, United States of America, of Calgon Center, Pittsburgh, 25, Pennsylvania, United States of America, do hereby declare the invention for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- The present invention relates to the removal of carbon dioxide and other acidic gases from hydrocarbon gases, nitrogen and the like neutral gases.
- It has been proposed in the past to remove carbon dioxide from ethylene gas by the selective absorption of the carbon dioxide on a molecular sieve. Typical patents showing such a procedure are U.S. Patent Nos. 3,078,637, 3,176,445, 3,242,641 and 3,266,221. However such a procedure is not as efficient as would be desired. Additionally such a procedure is relatively costly.
- The present invention seeks to provide an economical process for the removal of carbon dioxide from ethylene, and more generally, of acidic gases from neutral gases, and especially of relatively small amounts of carbon dioxide from larger amounts of neutral gases.
- According to the present invention, there is provided a process of removing an acidic gas from a mixture with a non-acidic gas comprising passing the gas mixture through granular activated carbon impregnated with monoethanolamine, the monoethanolamine being at least 10.5% by weight of the total of the activated carbon and the monoethanolamine.
- The invention can be used to remove carbon dioxide or other acidic gases such as nitrogen dioxide, sulphur dioxide, hydrogen sulphide, hydrogen cyanide, sulfur trioxide, COS, CS₂ and phosgene from such gases as flue gas, natural gas, coke oven gas, air, nitrogen, hydrogen, hydrocarbon gases such as ethane, propane or olefins, e.g., ethylene and propylene. It may also be used to remove acidic gases from cigarette, cigar and pipe smoke.
- The monoethanolamine impregnated activated carbon has a greater capacity for carbon dioxide removal from ethylene than has a molecular sieve, provided that the impregnated carbon contains at least 15% and up to 50% by weight of the total of activated carbon and monoethanolamine.
- In the present specification and claims the percentage of monoethanolamine is based on the total of the carbon and the monoethanolamine. Also, unless otherwise indicated, all parts and percentages in the specification are by weight.
- The results of the present invention are surprising since the activated carbon itself has no capacity for carbon dioxide removal at normal temperatures and when the monoethanolamine impregnated activated carbon is replaced by monoethanolamine impregnated silica gel or monoethanolamine impregnated alumina the product is ineffective for removal of carbon dioxide from ethylene.
- It was also found critical to use monoethanolamine as the impregnant since diethanolamine impregnated activated carbon and triethanolamine impregnated activated carbon were ineffective for removal of CO₂ from ethylene.
- The activated carbon should be granular so that it is effective as a support for the monoethanolamine. The particle size of the carbon may be from 4 to 325 mesh (U.S. sieve series). The activated carbon employed in the following examples was Pittsburgh type BPL 12 × 30 mesh, which is granular carbon of 12 × 30 U.S. sieve series mesh size with a density of 0.48 to 0.51 gms/cc, and a minimum hardness number of 90. It is made from selected grades of bituminous coal combined with suitable binders, and is obtainable from the Pitts-

[Price 4s. 6d.]

burgh Activated Carbon Company, Calgon Center, Pittsburgh, Pennsylvania, U.S.A.

5 Preferably the monoethanolamine is 18 to 35% since the best results are obtained in this range. If it is desired to keep a very low concentration of MEA in the off gases, the MEA preferably is not over 20% of the MEA carbon.

10 The monoethanolamine impregnated activated carbon has been used to remove carbon dioxide from ethylene at pressures from atmospheric up to 225 psig. The pressure is not critical. The monoethanolamine impregnated activated carbon has been employed to remove 15 40 to 570 ppm of CO₂ (by volume) in ethylene and to remove 6,700 ppm of carbon dioxide (by volume) in nitrogen. Normally, the carbon dioxide to be removed can be present in an amount of 5 ppm to 200,000 ppm based on the total volume of gas treated.

20 There are various ways of impregnating the activated carbon with the monoethanolamine (MEA). Thus, the MEA in liquid form may be sprayed as a fine spray mist on the activated carbon granules. Since no water is present such a method is considered a dry spray.

25 Alternatively the activated carbon may be sprayed with a wet spray, i.e. a mixture of MEA and water. While in the specific examples of the wet method set forth below there were used equal parts of the MEA and water it is possible to employ 1 to 99% of MEA, with the balance being water.

30 As another dry method of impregnation the activated carbon granules may be covered with liquid MEA and as another wet method the activated carbon granules may be covered with a solution of MEA in water (e.g. 50:50).

35 Still another procedure is to distil MEA vapor into the activated carbon granules. This latter method is described and claimed in our copending application No. 52338/67 (Serial No. 1157377).

40 The spray method is preferred to the soak method since there is no need to drive off water or carefully control drying. The vapor method is preferred over the spray method since it appears to give a product with a higher capacity for CO₂.

50 When MEA reacts with CO₂ in the presence of water, the reaction takes place on a mole for mole basis and the product is MEA carbonate. However, if no water is present

then 2 moles of MEA are required to react with one mole of CO₂ to form MEA carbamates. While this latter reaction is not as efficient, for some purposes it is essential that the effluent gas be anhydrous. In those cases, of course, the presence of water in impregnating the activated carbon is not desired since the water must be removed prior to use.

The reaction of ethanolamine to form the carbonate has generally been considered reversible but the reaction to form the carbamate has not been considered reversible.

The bed depth for the MEA impregnated activated carbon is not particularly critical. Above a bed depth of 6 inches, the capacity for CO₂ adsorption increases linearly. Preferably, the bed depth is at least 3 inches although it can be 1.5 inches or less with some sacrifice in efficiency at a linear gas velocity of 20 ft./min.

After the monoethanolamine impregnated activated carbon has been saturated with carbon dioxide it can be regenerated using the technique set forth in our aforementioned copending application.

In the present specification and claims the term "gas" includes vapors.

EXAMPLE 1

Samples of the said Pittsburgh type BPL 12 X 30 mesh activated carbon were dry sprayed with monoethanolamine. Sample (a) contained 14.9% MEA (based on the total of MEA and carbon), sample (b) contained 18.7% MEA, and sample (c) contained 27.5% MEA. These samples were made up into beds having a depth of 6 inches each. There also was prepared sample (d), which does not form part of the present invention, a similar 6-inch bed of a molecular sieve of mesh size 42/60 having a pore opening size of 5 angstroms conditioned overnight at 450°C. for comparison. Sample (a) had a weight of 13.2 grams; sample (b), 14.4 grams; sample (c), 16.3 grams; and sample (d), a weight of 15.2 grams.

Ethylene gas containing 350 ppm (by volume) of carbon dioxide at a pressure of 225 psig was passed through the beds at a rate of 15 liters per minute (measured at room temperature and atmospheric pressure). The effluent was tested for per cent carbon dioxide breakthrough. The results are set forth in Table 1.

TABLE 1

Sample (a)			Sample (b)			Sample (c)			Sample (d)		
Time (Min.)	Liters	% Break- through	Time (Min.)	Liters	% Break- through	Time (Min.)	Liters	% Break- through	Time (Min.)	Liters	% Break- through
2	30	0	6	90	0	1	15	0	4	60	0
9	135	0	11	195	0	7	105	0	10	150	0
15	225	19.7	20	300	0	13	195	0	16	240	0
21	315	55.4	27	405	0	19	285	0	36	540	91.1
28	420	78.8	36	540	1.5	25	375	0	47	705	98.2
35	525	90.6	42	630	20.0	37	555	0	52	780	99.0
41	615	92.2	49	735	48.5	43	645	0			
46	690	95.5	56	840	62.0	52	780	0			
			62	930	75.1	64	960	0			
			68	1020	79.0	80	1200	0			
			74	1110	84.0	108	1620	48.4			
			79	1185	87.4	114	1710	58.5			
			92	1380	92.7	125	1875	70.3			
						133	1995	71.4			
						141	2115	78.1			
						156	2340	83.3			
						165	2475	89.5			
						178	2670	91.6			
						197	2955	96.3			
						210	3150	97.3			

EXAMPLE 2

The procedure of Example 1 was repeated using sample (c) 27.5% MEA at bed depths of 1.5 inches (weight 3.5 grams) and 3 inches (weight 7.5 grams). The amount of CO₂ in

the ethylene was reduced to 325 ppm (by volume) and the gas flow rate was 15 liter/min. at 225 psig. The results are set forth in Table 2.

TABLE 2

Bed Depth Time (Min.)	1.5 inches Liters	(27.5% MEA) % Breakthrough	Bed Depth Time (Min.)	3 inches Liters	(27.5% MEA) % Breakthrough
2	30	0	2	30	0
8	120	5.9	7	150	0
13	195	27.7	13	195	0
18	270	48.5	19	285	0
23	345	62.3	25	375	21.1
27	405	69.3	30	450	39.4
33	495	77.7	37	560	54.1
38	570	82.2	43	645	63.1
44	660	85.6	48	720	72.9
50	750	90.3	54	810	74.3
55	825	90.3	59	885	82.7
66	990	92.1	70	1050	87.6
			75	1125	88.6
			80	1200	88.7
			85	1275	91.1

EXAMPLE 3

The procedure of Example 2 was repeated with sample (c) (27.5% MEA) using a bed

depth of 9 inches (weight 24.0 grams). The other conditions were identical with Example 2. The results are set forth in Table 3.

TABLE 3

Time (Min.)	Liters Test Gas	% Breakthrough
3	45	0
11	165	0
32	480	0
50	750	0
56	840	0
75	1125	0
91	1365	0
104	1560	0
120	1800	32.8
126	1890	50.5
132	1980	61.7
138	2070	70.1
145	2175	77.9
155	2375	82.4
164	2460	87.7
187	2805	93.1

EXAMPLE 4

The procedure of Example 1 was repeated and samples of the said 12 X 30 mesh activated carbon were dry sprayed with commercial grade monoethanolamine. Sample (f) contained 10.5% MEA and sample (g) contained 27.7% MEA. The samples were made

into beds having a depth of 6 inches each. Sample (f) weighed 12.0 grams and sample (g) 14.4 grams. Ethylene gas containing 375 ppm (by volume) of carbon dioxide at a pressure of 225 psig was passed over the beds at a rate of 15 liters/min. at room temperature. The results are set forth in Table 4.

10

15

TABLE 4

Sample (f) 10.5% MEA			Sample (g) 27.7% MEA		
Time (Min.)	Liters	% Break- through	Time (Min.)	Liters	% Break- through
3	45	0	3	45	0
13	195	0	13	195	0
19	285	0	40	600	0
26	390	46.7	51	765	0
31	465	67.2	61	915	0
41	615	87.6	71	1065	0
51	765	90.5	81	1215	13.4
71	1065	98.5	86	1290	21.9
			91	1365	30.8
			105	1575	47.3
			117	1755	57.2
			122	1830	59.7

EXAMPLE 5

The procedure of Example 4 was repeated but the carbon was sprayed with the commercial MEA to obtain sample (h) containing

39.98% MEA. The 6-inch bed weighed 17.5 grams. The results in regard to CO₂ break-through for sample (h) are shown in Table 5.

TABLE 5

Time (Min.)	Liters Test Gas	% Breakthrough
4	60	0
10	150	0
34	510	0
52	780	0
65	975	0
71	1065	0
81	1215	0
104	1565	18.9
110	1650	26.8
116	1740	35.3
122	1830	40.7
127	1905	44.3
138	2070	51.7
143	2145	56.2
163	2445	66.1
169	2535	68.7
175	2625	68.7

EXAMPLE 6

37 grams of technical grade monoethanolamine and 37 grams of water were mixed and added to 100 grams of the BPL activated carbon. The impregnated carbon was dried in a steam carbinet at 68°C. The dry activated carbon contained 37 grams of MEA which was 27% MEA based on the total of MEA and carbon. This product was sample (i). Sample (j) was prepared by dry spraying

the activated carbon with 27% MEA and sample (k) was prepared by dry spraying the activated carbon with 13% technical MEA. Tests were run as before at 225 psig at 15 liter/min. with ethylene gas containing 325 ppm (by volume) of CO₂. The beds had a depth of 6 inches. Samples (i) and (j) each weighed 14.8 grams and sample (k) weighed 12.6 grams. The results are set forth in Table 6.

TABLE 6

Sample (i)			Sample (j)			Sample (k)		
Time (Min.)	Liters	% Break- through	Time	Liters	% Break- through	Time	Liters	% Break- through
12	180	0	20	300	0	7	105	0
35	525	0	39	585	0	15	225	0
46	690	0	56	840	0	21	315	0
58	870	1.5	67	1005	0	26	380	0
62	930	6.9	82	1230	5.4	35	525	17.4
72	1080	24.9	93	1395	20.3	41	615	38.1
83	1245	43.0	104	1560	32.8	45	685	60.1
100	1500	60.0	120	1800	48.1	50	750	67.8
121	1815	66.3	131	1965	57.5			

EXAMPLE 7

Samples of the said Pittsburgh type BPL 12 X 30 mesh activated carbon were dry sprayed with MEA. In one case CP monoethanolamine was used to obtain sample (l) (weight 15.1 grams) containing 27% MEA and in the other case technical grade monoethanolamine was employed to obtain sample (m) (weight 14.8 grams) containing 27% MEA. Tests were run as before at 275 psig at 15 liter/min. with ethylene gas containing 570 ppm (by volume) of CO₂. The beds had a depth of 6 inches. The results are set forth in Table 7.

TABLE 7

Sample (l)			Sample (m)		
Time (Min.)	Liters	% Break- through	Time (Min.)	Liters	% Break- through
8	120	0	7	105	0
25	375	0	12	180	0
37	555	0	18	270	0
47	705	2.0	35	525	0
52	780	11.4	47	705	26.5
62	930	34.9	57	855	48.8
68	1020	45.8	72	1080	68.2
74	1110	51.1			

EXAMPLE 8

The procedure of Example 7 was repeated with the following modifications. The granular activated carbon was impregnated with 13% of technical MEA to produce sample (n) and

the polyethylene test gas contained only 42 ppm (by volume) of CO₂. The 6-inch bed weighed 12.6 grams. The results are set forth in Table 8.

TABLE 8

Sample (n)

Time (Min.)	Liters Test Gas	% Breakthrough
18	270	0
52	780	0
61	915	0
128	1920	0
158	2370	0
217	3755	0
234	3510	3.7
252	3780	7.5
265	3975	11.2
284	4260	20.1
305	4575	35.8
320	4800	44.8
353	5295	56.7

EXAMPLE 9

A sample was prepared by dry spraying the activated carbon with MEA to obtain a product containing 13% MEA. This product was divided into sample (o) and sample (p). A sample was prepared by wet spraying the activated carbon with a mixture of equal parts by weight of MEA and water. The product was sample (q) which contained 13% MEA and 13% water.

Ethylene containing 270 ppm (by volume) of CO₂ was passed through 6-inch beds of the samples. Sample (o) weighed 12.84 grams, sample (p) weighed 13.08 grams and sample (q) weighed 15.21 grams. The ethylene was bubbled through water before being passed through sample (p) but the ethylene was dry before being passed through samples (o) and (q). In each case the ethylene was flowed at a rate of 1 liter/min. and at atmospheric pressure (i.e., about 760 mm.). Samples (o) and (p) had identical curves. Both showed no breakthrough until 270 liters of gas had passed,

at 350 liters there was a 3% breakthrough and at 410 liters there was an 86% breakthrough. Sample (q) did not show any breakthrough until 680 liters of gas had a 3% breakthrough at 700 liters and a 90% breakthrough at 780 liters. Thus, in accordance with what was expected sample (q) containing water had twice the capacity of the other two samples.

EXAMPLE 10

This example illustrates the outstanding results employing the vapor phase impregnation technique claimed in our aforementioned co-pending application.

Monoethanolamine was boiled and the vapors used to impregnate BPL activated carbon. The product was sample (r) which contained 27% MEA. It was employed in a 6-inch bed which weighed 15.1 grams. It was tested with ethylene gas containing 270 ppm (by volume) of CO₂ at a pressure of 225 psig and a flow rate of 15 liters/min. The results are set forth in Table 9.

TABLE 9

SAMPLE (r)

Time (Min.)	Liters Test Gas	% Breakthrough
2	30	0
20	300	0
37	555	0
53	795	0
60	900	0
75	1175	0
83	1245	0
90	1350	0
97	1455	0
110	1650	0
122	1830	0
128	1920	1.5
135	2025	4.5
141	2115	9.9
148	2220	18.3
157	2355	61.6

WHAT WE CLAIM IS:—

1. A process of removing an acidic gas from a mixture with a non-acidic gas comprising passing the gas mixture through granular activated carbon impregnated with monoethanolamine, the monoethanolamine being at least 10.5% by weight of the total of the activated carbon and the monoethanolamine.
2. A process as claimed in claim 1 wherein the monoethanolamine is at least 15% by weight of the total of the activated carbon and the monoethanolamine.
3. A process according to claim 1 or claim 2 wherein the non-acidic gas is flue gas, natural gas, coke, oven gas, air, nitrogen, hydrogen or gaseous hydrocarbons.
4. A process according to any of claims 1—3 wherein the non-acidic gas is an olefin.
5. A process according to claim 1 or claim 2 wherein the acidic gas is CO_2 .
6. A process according to claim 5 where-

in the non-acidic gas is a gaseous hydrocarbon.

7. A process according to claim 1 wherein the non-acidic gas is ethylene.

8. A process according to claim 7 wherein the acidic gas is CO_2 .

9. A process according to claim 8 wherein the granular activated carbon is from 4 to 325 mesh (U.S. Sieve series) and the monoethanolamine is 10.5 to 50% by weight of the total of the monoethanolamine and activated carbon.

10. A process according to claim 9 wherein the monoethanolamine is 18 to 35% by weight of the total of monoethanolamine and activated carbon.

11. A process according to any preceding claim wherein the mixture is cigarette or cigar or pipe smoke.

12. A process of removing an acidic gas from a mixture with a non-acidic gas substantially as hereinbefore described in the Examples.

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